ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF TRIS ACETAMIDE MODIFIED SULFONAMIDE BASED RESIN FOR REMOVING MERCURY SALTS FROM AQUEOUS SOLUTIONS

M.Sc. THESIS

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509131021

Department of Chemistry

Chemistry Programme

Thesis Advisor: Prof. Dr. B. Filiz ŞENKAL

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

TRİS ASETAMİD MODİFİYE ÇAPRAZ BAĞLI SÜLFONAMİD ESASLI REÇİNENİN SENTEZİ VE CIVA TUZLARININ SULU ORTAMLARDAN UZAKLAŞTIRILMASINDA KULLANILMASI

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To my family,

FOREWORD

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Chemist

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ABBREVIATIONS

CSPS	**:** Chlorosulfonated Polystyrene
DVB	**:** Divinyl Benzene
FT-IR	**:** Fourier transform infrared spectroscopy
D-R	**:** Dubinin–Radushkevich
WHO	**:** World Health Organization
GI	**:** Gastrointestinal
BEE	**:** Bipolar Electrolyte Exchange
UV	**:** Ultraviolet
PE	**:** Polyethylene
PP	**:** Polypropylene
PTFE	**:** Polytetrafluoroethylene
PGMA	**:** Poly (glycidyl methacrylate)
PS	**:** Polystyrene
EDTA	**:** Ethylenediaminetetraacetic acid

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SYNTHESIS OF TRIS ACETAMIDE MODIFIED SULFONAMIDE BASED RESIN FOR REMOVING MERCURY SALTS FROM AQUEOUS SOLUTIONS

SUMMARY

In this study, crosslinked chlorosulfonated polystyrene resin (CSPS) was prepared starting from crosslinked polystyrene-divinyl benzene (DVB) resin. The CSPS was reacted with excess tris (2-aminoethyl) amine to obtain resin1.

And then, the resin 1 was amidated with excess of acetyl chloride to obtain sulfonamide based tris amide containing resin (resin 2).

Resin 1 and Resin 2 were characterized by using analytical methods and FT-IR.
$HgCl_2$ was used in mercury adsorption experiments. The mercury sorption capacities of the sorbent were determined by mixing weighed amount of polymer sample (0.1 g) with 10 mL aqueous Hg (II) solutions (0.1-0.00625 M). The mercury loading capacities were calculated from the initial and final Hg (II) contents of the solutions.

Also, the resin 2 was interacted with $HgCl_2$ depending on pH. According to the results obtained mercury adsorption capacity of the resin increased by increasing pH. Mercury sorption capacity of the resin 2 was found as 4.33 mmol/g resin at pH=6. Because of proton releasing during the binding, pH values closer to neutral condition are much favorable.

Sorption capacities of the other metal ions were studied and sorption capacity was found between 2.20-1 mmol/g resin.

Batch kinetic sorption experiment was performed by using $HgCl_2$ solution ($1.0x10^{-4}$ M).

The rate constant of adsorption was studied with the help of the pseudo-first-order rate expression of Lagergren model and the pseudo-second-order kinetic rate expression of Ho and McKay. The pseudo-first-order equation assumes that the adsorption rate decreases linearly as the adsorption capacity increases, which is suitable especially for low concentrations.

Also, the pseudo-second-order kinetic model assumes that the rate limiting step is the interaction between two reagent particles.

To examine the nature of the diffusion process for the adsorption of mercury onto the resin attempts were made to calculate the pore diffusion coefficients as intra-particle transport is supposed to be the rate-controlling step.

According to result of the kinetic models, the pseudo-first-order kinetic model having a low value for R^2, does not present a good fit with experimental data. In contrast, in the case of pseudo-second-order kinetic model, the high values of correlation coefficients showed that the data fitted well to the pseudo-second-order rate kinetic.
Adsorption isotherm models were applied. Three theoretical isotherm models Langmuir, Freundlich and Dubinin–Radushkevich were used to analyze the experimental data.

One of the most widely used isotherm equations for modeling adsorption data is the Langmuir equation. Based on the Langmuir equation; *C*e is the equilibrium concentration of mercury in solution (mmol/L), q_e is the equilibrium amount of mercury adsorbed on the beads at time *t* (mmol/g). q_m is the maximum adsorption capacity of the beads (mmol/g) and *b* (i.e., the adversely of dissociation constant of the ligand/surface interaction, K_d, or equal to association constant, K_a, ($b = K_a = (1/K_d)$) is the energy of adsorption dissociation constant.

The Freundlich expression is an empirical equation based on adsorption on a heterogeneous surface. Based on the Freundlich equation; K_F and *n* are the Freundlich constants characteristic of the system. K_F and *n* are indicator of the adsorption capacity and adsorption intensity, respectively. The slope and the intercept of the linear Freundlich equation are equal to $1/n$ and $\ln K_F$, respectively.

The linear plots of ln *q* versus ln *C* showed that the Freundlich isotherm can be representative for the mercury adsorption. The magnitude of K_F and *n* values of Freundlich model showed easy uptake of mercury from aqueous medium with a high adsorption capacity of the beads at room temperature. Values of $n>1$ for affinity beads indicates positive cooperativity in binding.

The Dubinin–Radushkevich (D–R) isotherm is also widely used in adsorption studies because it does not assume a homogeneous surface or constant adsorption potential.

The Dubinin–Radushkevich (D–R) constant can give the valuable information regarding the mean energy of adsorption. The adsorption behavior might be predicted the physical adsorption in the range of 1–8 kJ/mol of the mean adsorption energies (*E*), and the chemical adsorption in more than 8 kJ/mol of the mean adsorption energies (*E*), respectively. *E* value was calculated as 2.016 kJ/mol for mercury, and found to be in the range of a typical free energy attributed to physical adsorption. So, the D–R isotherm also is a model which describes the experimental data compared to other applied isotherm models.

TRİS ASETAMİD MODİFİYE ÇAPRAZ BAĞLI SÜLFONAMİD ESASLI REÇİNENİN SENTEZİ VE CIVA TUZLARININ SULU ORTAMLARDAN UZAKLAŞTIRILMASINDA KULLANILMASI

ÖZET

Bu çalışmada, çapraz polistiren-divinyl benzen (DVB) reçineden başlayarak çapraz klorosülfonlanmış polistiren reçine (CSPS) hazırlanmıştır.

Çapraz bağlı poli (stiren-divinil benzen (DVB)) kürecikler süspansiyon polimerizasyonu ile hazırlanmıştır. Burada sürekli faz olarak su, stabilizatör olarak arap zamkı, başlatıcı olarak dibenzoil peroksit, çapraz bağlayıcı olarak DVB, gözenek yapıcı olarak tolüen ve monomer olarak stiren kullanılmıştır.

Daha sonrasında PS-DVB reçine klorosülfonik asitin aşırısı ile reaksiyona sokulmuştur.

Oda sıcaklığında 24 saat bekletildikten sonra vakumda süzülüp diklormetan, aseton ve buzlu su ile yıkandıktan sonra tekrar aseton ve eter ile yıkanıp vakumda oda sıcaklığında kurutuldu.

Klorosülfonlanmış PS, tris (2-aminoethyl) Aminin aşırısı ile etkileştirilmiştir. Reaksiyona 24 saat oda sıcaklığında ve 5 saat 60 derecede devam edildikten sonra karışım soğuk suya dökülüp süzülüp önce su sonra da etanol ile yıkanıp vakumda kurutulmuştur. Bu işlemlerin sonucunda reçine 1 elde edilmiştir.

Sonra reçine 1 Sülfonamid esaslı tris amid içeren reçine (reçine 2) elde etmek için asetil klorür fazlası ile etkileştirilmiştir.

Reçine 1 ve reçine 2 FT-IR ve analitik yöntemler kullanılarak karakterize edilmiştir.

Cıva adsorpsiyon deneylerinde $HgCl_2$ kullanılmıştır. Adsorbentin civa tutma kapasitesi polimer örneğinin bilinen bir miktarı (0,1 g) ile farklı konsantrasyonlarda (0,1, 0,05, 0,025, 0,0125, 0,00625M) 10 ml Hg(II) çözeltileri karıştırılarak ölçülmüştür. Hg (II) çözeltilerinin reçine ile etkileşmeden önce ve etkileştikten sonraki konsantrasyonları difenil karbazid kullanılarak kolorimetrik yöntemlerle analiz edilmiştir. UV – Vis spektrofotometresi ile 542.00 nm' de analizler yapılmıştır.

Cıva tutma kapasiteleri, başlangıç ve son Hg(II) çözeltileri ile hesaplanmıştır.

Ayrıca, reçine 2 farklı pH' lara (pH=2, 4, 5, 6) bağlı olarak $HgCl_2$ ile etkileştirilmiştir. Buradan elde edilen sonuçlara göre; reçinenin cıva adsorpsiyon kapasitesi pH' ın artması ile artmıştır. pH 6' da reçine 2' nin cıva adsorpsiyon kapasitesi 4,33 mmol/g reçine olarak bulunmuştur. Bağlanma sırasında proton bırakıldığından dolayı, pH değerinin nötral duruma yakın olduğu durumlar daha uygundur.

Reçine 2 nin adorpsiyon kapasitesi başka metal iyonları (Hg(II), Cd(II), Mg(II), Pb(II), Fe(III)) kullanılarak da hesaplanmıştır. Buna göre adsorpsiyon kapasitesi 1 ile 2,20 mmol/g reçine arasında bulunmuştur.

Reçine 2 için kinetik çalışma yapılmıştır. Kinetik denemeleri $1x10^{-4}$ M $HgCl_2$ çözeltisi ile yapılmıştır. Reaksiyon karışımından belirli zaman aralıklarıyla alınan numunelerden kolorimetrik olarak cıva konsantrasyonu belirlenmiştir.

Adsorpsiyon hız sabiti 2 modelden yararlanılarak hesaplanmıştır; Lagergren model , olarak bilenen pseudo birinci dereceden hız denklemleri ve Ho ve McKay modeli , olarak bilinen pseudo ikinci mertebeden hız denklemleridir.

Pseudo birinci mertebeden hız denklemi adsorpsiyon kapasitesinin artışıyla adsorpsiyon hızının lineer olarak düşmesini gösterir ve özellikle düşük konsantrasyonlar için kullanım alanı vardır.

Pseudo ikinci mertebeden hız denklemi iki reaktif parçacık arasında etkileşimlerin olduğunu ve etkileşimde hızı kısıtlayan bir adım olduğunu varsayar.

Partikül içi difüzyon modeli Weber ve Morris tarafından geliştirilmiştir. Difüzyon işleminin doğal yapısından kaynaklanan cıvanın reçine üzerine adsorpsiyonu sırasında oluşan girişimleri incelemek için gözenek difüzyon kat sayalarının hesaplanmasında "intra-particle" taşıma oranının, kontrol basamağı olduğu varsayılır.

"Intra Particle" eşitliğine bakacak olursak , k_i partikül içi difüzyon hız sabiti (mg/g. dak^2), C adsorbent ile adsorbat arasında oluşan tabakanın kalınlığı hakkında bilgi veren bir sabittir. Hız sabiti k_i, q_t'nin $t^{1/2}$ karşı çizilen grafiğinin eğiminden hesaplanırken C kesim noktasından hesaplanır.

Yapılan kinetik modellerinin sonuçlarına göre, pseudo birinci dereceden kinetik model R^2 için düşük bir değer vermiştir ve deneysel verilerle iyi bir uyum göstermemiştir. Bunun tersi olarak pseudo ikinci dereceden kinetik modelden elde edilen yüksek katsayı değerleri, deneysel verilerin bu model için uygun olduğunu göstermiştir. Bu tipik bir kimyasal adsorpsiyon modelidir

Adsorpsiyon izoterm modelleri uygulandı. Üç teorik izoterm modeli olan Langmuir, Freundlich ve Dubinin-Radushkevich, deneysel verilerin analizlerinde kullanıldı.

Adsorpsiyon verilerinin modellenmesinde en çok kullanılan izoterm Langmuir eşitliğidir. Langmuir eşitliğinde; *C*e (mmol/L) cıvanın çözeltideki denge konsantrasyonunu, q_e (mmol/g) zamana bağlı olarak (t) küreciklere adsorplanan cıva miktarını ve *b (* ligant/yüzey etkileşiminin dağılım katsayısı K_d ya da denge sabiti K_a, $b = K_a = (1/K_d)$) ise adsorpsiyon dağılma enerjisinin katsayısını tanımlamaktadır.

Formülde yer alan K_L (L/mg) değeri Langmuir sabitini, C_0 (mg/L) değeri ise absorblanan başlangıç konsantrasyonunu göstermektedir. Bu eşitlikten elde edilen R_L değeri reaksiyonun adsorpsiyona uygun olduğunu gösterir.

Eğer $R_L > 1$ ise reaksiyonun adsorpsiyona uygun olmadığını, $R_L = 1$ ise reaksiyonun lineer, $0 < R_L < 1$ değer aralığında ise reaksiyonun adsorpsiyona uygunluğundan söz edilebilir. Eğer $R_L = 0$ ise reaksiyonun geri dönüşümlü olduğu söylenebilir.

Yapılan çalışma sonucunda R_L değeri 0 ile 1 arasında çıkmıştır. Bu sonuçtan yola çıkarak reaksiyonun adsorpsiyona uygun olduğunu söyleyebiliriz.

Freundlich izotermi, heterojen yüzeyde meydana gelen fiziksel ve tersinir olabilen bir adsorpsiyonu tanımlar. Freundlich eşitliğinde, C_e: Denge anında çözeltide adsorplanmayan maddenin konsantrasyonu (mg/L), q_e: Denge anında birim

adsorbent üzerine adsorblanan madde miktarı (mg/g), K_F: Deneysel olarak hesaplanan adsorpsiyon kapasitesi, n: Adsorpsiyon şiddeti'dir Bu eşitlikte; K_F ve n sistemin karakteristik Freundlich sabitleridir. Eğim ve lineer Freundlich eşitliğinin kesişimi sırasıyla eşitlikte yer alan $1/n$ ve K_F değerlerini verir.

ln q' nun ln C' ye karşı doğrusal grafiğinin çizilmesi, Freundlich izoterminin cıva adsorsiyonu için uygunluğunu gösterir. Freundlich modelinde yer alan K_F ve n değerlerinin büyüklükleri, oda sıcaklığında kürelerin yüksek adsorpsiyon kapasitesi ile sulu ortamdan kolayca cıva alımını göstermektedir. n>1 ise kürelerin afinitesi bağlanmada pozitif bir etki gösterir.

Bu çalışmada Freundlich modelinden yola çıkarak yapılan hesaplamalar onucunda n değeri 1,126 bulunmuştur. Bu sonuca dayanarak Freundlich modelinin uygunluğundan sözedebiliriz.

Dubinin-Radushkevich (D-R) izoterm modeli de sıklıkla adsorpsiyon çalışmalarında kullanılır, çünkü homojen bir yüzey veya sabit bir adsorpsiyon potansiyeli varsayımında bulunmaz.

D-R izoterminin deneysel verileri açıklayan bir model olduğunu söyleyebiliriz. Bu varsayımdan yola çıkarak D-R denkleminde bulunan terimler şu şekildedir; B_{DR} değeri izoterm sabitidir.

Bu arada ε değeri; R, T ve C_e sırasıyla gaz sabiti (8.314 J/mol K), mutlak sıcaklık (K) and adsordsiyon denge sabiti değerleri ile hesaplanır.

D-R izotermi adsorbentin poroz yapısıyla ilgilidir ve adsorpsiyonun fiziksel ya da kimyasal olması ile ilgili bilgi verir. D-R izoterminde adsorbatın molekülü başına ortalama adsorpsiyon enerjisini ifade eden E değeri adsorpsiyonun fiziksel ya da kimyasal olup olmadığı hakkında bilgi verir.

Dubinin-Radushkevich (D-R) sabiti adsorpsiyonun ortalama enerjisi konusunda önemli bilgi veren adsorpsiyon enersijsi (E) 1-8 kJ/mol aralığında ise fiziksel adsorpsiyon, eğer enerji 8 kJ/mol değerinden yüksek ise kimyasal adsorpsiyondur.

Deneysel verilerden cıva için E değeri 2,016 kJ/mol olarak bulundu ve fiziksel adsorpsiyon için belirtilen serbest enerji aralığında olduğu bulunmuştur.

1. INTRODUCTION

The quality of our environment is getting worse day by day with the largest cities reaching saturation points and unable to cope with the increasing pressure on their infrastructure. Industrial effluents, sewage and farm wastes are the major pollutants contaminating the environment. Most of the industries discharge wastewater and their effluents containing toxic materials into rivers without adequate treatment [1].

Heavy metals are major pollutants in marine, ground, industrial and even treated wastewater. Most of the point sources of heavy metal pollutants are industrial wastewater from mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber and wood products. The heavy metals are transported by runoff water and contaminate water sources downstream from the industrial site (Figure 1.1). To avoid health hazards it is essential to remove these toxic heavy metals from waste water before its disposal. Most of the heavy metals discharged into the wastewater are found toxic and carcinogenic and cause a serious threat to the human health [1].

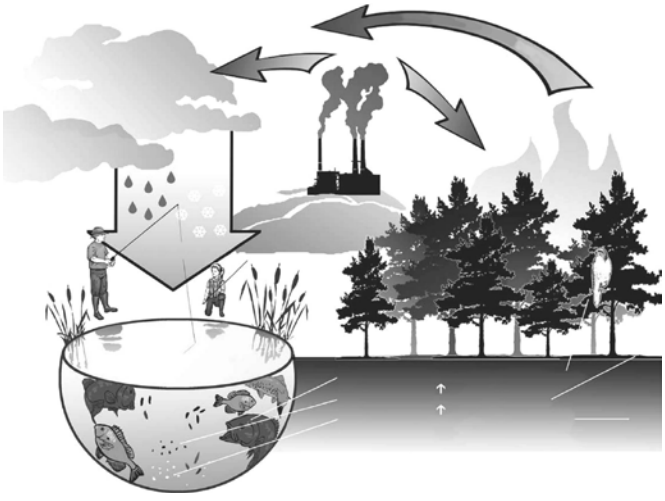

Figure 1.1 The mercury cycle [2]

Mercury is categorized as an extremely toxic substance. Mercury occurs naturally in the environment and exists in several forms [3]. Elemental mercury is used in many industrial processes and manufactured products, including but not limited to, manufacture of soaps, detergents, and fluorescent bulbs, in production of sulphuric acid, in gold mining, in batteries and soon. All forms of mercury, namely, metallic or elemental forms as used in dentistry for the manufacture of dental silver amalgam during restorative dentistry; organic forms as existing in fish, pesticides and other bonded-chemicals and inorganic mercury, at times mercuric oxide used as the red coating for traditional herbal remedies, are present in our human environment through usage. Consequently mercury is present in our human environment from manufacturing to waste disposal and finally as waste in our midst. This mercury could be in the air we breathe, in the food we consume, also in antiseptics or antifungals we come in contact with daily as hand wash etc. [4].

The use of polymer-bonded ligands in selective mercury removal has been the subject of many research articles [5, 6] and reviews [7, 8]. Because of the high toxicity of all mercury compounds, the extraction of mercuric ions from aqueous wastes and drinking water is of special environmental importance. Two common ligand types, sulfur and amide, are being used currently in the design of polymer sorbents for binding mercuric ions selectively. One of the important ligating group for selective mercury binding is the amide group, which forms covalent mercury–amide linkages under ordinary conditions. The amide group has less of a tendency to bind with other metal ions under the same conditions because of the weak electron-donating nature of the amide group. As a result, the amide ligand is unique in its selective mercury uptake [9].

In this study, new polymeric resin with polystyrene-based polymeric sorbents containing sulfonamides has been prepared for removal of mercuric ions. Mercury sorption characteristics and regeneration conditions of the resulting resins have been studied and also sorption capacities of sorbents and kinetic measurements of sorption. Affinity of the resins for other metal ions such as Cd (II), Mg (II), Pb (II) and Fe (III) have been also investigated.

2. THEORETICAL PART

2.1 Toxic Metal Ions and Their Harms

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0.Most of the heavy metals are dangerous to health or to the environment. Heavy metals in industrial wastewater include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Acute heavy metal intoxications may damage central nervous function, the cardiovascular and gastrointestinal (GI) systems, lungs, kidneys, liver, endocrine glands, and bones. Chronic heavy metal exposure has been implicated in several degenerative diseases of these same systems and may increase the risk of some cancers [1].

Table 2.1 Sources and toxicological effects of some heavy metals [10]

Heavy Metal	**Sources**	**Effects**
Copper	Water pipes; Copper water heaters; Frozen greens and canned greens using copper to produce an ultra -green color, Alcoholic beverages from copper brewery equipment; Instant gas hot water heaters; Hormone pills; Pesticides. insecticides; fungicides; Copper jewelry; Copper cooking pots	Mental disorders, Anaemia; Arthritis/rheumatoid arthritis; Hypertension, Nausea/vomiting, Hyperactivity, Schizophrenia**,** Insomnia**,** Autism**,** Stuttering**,** Postpartum psychosis**,** Inflammation and enlargement of liver, heart problem**,** Cystic fibrosis.
Chromium	Steel and textile industry	Skin rashes, respiratory problems, haemolysis, acute renal failure, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer.

Table 2.1 (Continue) Sources and toxicological effects of some heavy metals [10]

Heavy Metal	Sources	Effects
Nickel	Effluents of silver refineries, electroplating, zinc base casting and storage battery industries.	Dermatitis, Myocarditis, Encephalopathy, pulmonary fibrosis, cancer of lungs, nose and bone, headache, dizziness, nausea and vomiting, chest pain, rapid respiration.
Lead	Industries such as mining, steel, automobile, batteries and paints. Pollutants arising from increasing industrialization	Nausea, Encephalopathy, Headache and vomiting, Learning difficulties, Mental retardation, Hyperactivity, Vertigo, kidney damage, Birth defects, Muscle weakness, Anorexia, Cirrhosis of the liver, Thyroid dysfunction, Insomnia, Fatigue, Degeneration of motor neurons, Schizophrenic like behaviour.
Mercury	Industries like chloro-alkali, paints, pulp and paper, oil refining, rubber processing and fertilizer, batteries, dental fillings adhesives, fabric softeners, drugs, thermometers, fluorescent light tubes and high intensity street lamps, pesticides, cosmetics and pharmaceuticals	Tremors, Birth defects, Kidney damage, Nausea, Loss of hearing or vision, Gingivitis, Chromosome damage, Mental retardation, Tooth loss, Seizures, Cerebral palsy , Blindness and deafness, Hypertonia – muscle rigidity, Minamata disease.

2.1.1 Mechanism of Toxic Effect

Nearly 2500 years ago, Hippocrates described the toxic effects of numerous poisons including lead, mercury, and arsenic. In the Middle Ages, the art of poisoning and the study of toxic effects became a formidable science in the hands of Catherine de Medici, who reported on the use of poisons, their clinical signs and symptoms, their potency, site of action, and how rapidly they produced their effects [11]. Today, we know that the toxic actions of pollutants vary dramatically based on dose, the length of exposure, and individual response. In fact, the symptoms that develop among a group of people exposed to the same toxic substance may vary so much as to appear to be caused by completely different substances. A toxin can produce a harmful effect upon an organ by either stimulating or depressing the normal metabolic actions of that particular organ. Very small amounts of toxic agents have the ability to stimulate function(s) in a variety of organs, whereas larger doses may impede or

even destroy the activity of the organ involved. The body is able to detoxify foreign substances principally through the liver, and other organs such as the kidneys, intestines, and lungs. Sometimes adverse effects occur when the quantity of the toxic substance in the body overwhelms the body's detoxification mechanisms or when injury or illness has compromised the body's ability to detoxify substances. The harmful effects of environmental toxins are dominated by three principal mechanisms which include: the toxins influence on enzymes; direct chemical combination of the toxin with a cell constituent; and secondary action as a result of the toxins presence in the system [12].

2.1.2 Mercury

There are three different forms in which mercury is found in the environment: elemental mercury vapor, inorganic mercury compounds and organic (usually methyl) mercury. The three different forms are significantly different from one another. They are each absorbed by the body differently, they are used and manufactured for different purposes and they have different effects on reproduction and development [13].

Mercury is used in the production of chlorine, and in the production of mercury thermometers, batteries, and fluorescent light bulbs. Mercury is also a constituent of dental amalgams. Concerns regarding mercury stem from its volatile nature, resulting in global dispersal throughout the air and water. To make matters even worse, inorganic mercury may be methylated by microorganisms which are present naturally in the environment to an even more toxic form, methyl mercury, which tends to bio-accumulate in marine life [14].

Debate continues about the lowest levels at which mercury causes human health effects. Studies have found that the health effects of organic mercury are similar in both animal and human populations. Studies in mice have shown that cells in the developing brain stop in the middle of cell division when exposed to organic mercury [13].

Organic mercury is the most toxic form of mercury due to its ease of oral absorption while circulating in the bloodstream, crossing the blood brain-barrier, and destroying the very cells which control coordination. Symptoms of poisoning appear 1 to 2

months after exposure, showing initial symptoms like numbness of the tongue, lips and fingertips. Speech gradually becomes slurred, and difficulty swallowing soon follows [15]. Previously it was believed that mercury, as a heavy metal, would settle to the bottom of lakes and rivers and would be harmlessly buried there, covered by sand. However, certain microorganisms convert mercury metal to organic mercury compounds, mainly methylmercury and dimethylmercury. Dimethylmercury evaporates quickly from the water, but methylmercury remains in the bottom sediments and is slowly released into the water, where it enters organisms in the food chain and is biologically magnified (by buildup of chemical elements or substances in organisms in successively higher trophic levels). Methylmercury is concentrated in fish, and people who eat the contaminated fish can get mercury poisoning [2]. The most infamous episode of mass poisoning occurred during the years 1953-1961 in the town of Minamata on the Japanese island of Kyushu. A local vinyl chloride manufacturing facility had been dumping inorganic mercury waste into the Minamata Bay where bacteria in the sediment converted it into organic mercury which then moved through the aquatic food chain, contaminating the fish. The fish showed concentrations of mercury 100,000 times that of the water levels. The population of Minimata relied heavily on a fish diet and vividly recall the day when the cats started acting weirdly and hurling themselves into the ocean to die. Then in 1956, people started showing the symptoms of central nervous system damage including tremors, convulsions, numbness of hands and feet, losses in speech, hearing and vision [16]. In many cases of mercury poisoning, a pregnant mother will remain relatively free of symptoms while children born to her will demonstrate gross physical abnormalities and severe mental retardation (Figure 2.1) [14, 16].

Figure 2.1 Minamata disease [17]

More than 1,000 Minamata Bay sufferers have since died. Minamata's population has shrunk since the time of the poisoning from 50,000 to less than 33,000. The chemical company (Chisso Corporation) implicated in this disaster did not stop dumping until 1968. More than forty years later, the prefectural government has declared that the fish in Minimata Bay now meet safety standards and the net that confined the fish to the bay has been removed. However, the social stigma and discrimination for victims of Minimata will likely continue [16]. By 1991, more than 2000 cases of Minamata disease had been confirmed. A similar epidemic occurred again, in 1965, but this time in riverside villages along the Agano River, Niigata, Japan [14].

Elemental mercury is the type of mercury which is found in dental amalgam fillings, thermometers and batteries. It is hazardous only when inhaled. Due to its low vapor pressure, it can be inhaled at room temperature. Elemental mercury can easily pass the blood-brain barrier and cross the placenta to the fetus once it is in the body. Individuals can be exposed to mercury in the air from waste incinerators that burn medical waste or batteries, and also from oil and coal burning, since mercury is a contaminant of these fuels [18]. It is far more dangerous to inhale mercury fumes than to swallow elemental mercury, such as the mercury which is found in an oral thermometer. If swallowed, the mercury passes through the gastrointestinal tract and is excreted in a few short days.

Inorganic mercury vaporizes at room temperature and its volatility increases markedly with each degree increase in temperature. This makes it especially hazardous when spilled on floors or surfaces where dirt or grease may exist and combine with the mercury to form tiny drops that expose larger surface areas to air. Vaporized inorganic mercury can enter the body either by inhalation or absorption through the skin following prolonged contact. Symptoms may include damage to kidney tubules, liver damage, and interference with coordination, generalized tremors, and possible hallucinations. These symptoms are described among hat makers in 17th century France who soaked animal hides in a solution of mercuric nitrate in order to soften the hairs. This practice allowed for frequent contact of the hat makers' arms and hands to be in contact with a solution of inorganic mercury, and they developed the typical symptoms of inorganic mercury poisoning referred to as "Mad Hatters' Disease" (Figure 2.2) (featured in the children's story, Alice in Wonderland [15,19]. Decreased performance on memory tests and verbal concept formation has also been documented in industry workers exposed to mercury vapor. Neurotoxic effects such as dizziness, weakness, insomnia, numbness, and tremor were observed in a 12-year-old girl exposed to spilled mercury. [19]

Figure 2.2 The Mad Hatter [19]

2.2 Ion Exchange

Among different techniques used for removal of high concentrations of heavy metals, precipitation-filtration, ion exchange, reverse osmosis, oxidation-reduction, solvent extraction, as well as membrane separation should be mentioned [20, 21].

Ion exchange may be defined as the exchange of ions between the substrate and surrounding medium. The most useful ion exchange reaction is reversible. When the reaction is reversible, the ion exchanger can be reused many times. Generally resins are manufactured in the spherical, stress and strain free form to resist physical degradation. They are stable at high temperatures and applicable over a wide pH range. Ion Exchange resins, which are completely insoluble in most aqueous and organic solutions, consist of a cross linked polymer matrix to which charged functional groups are attached by covalent bonding [22]. The ion exchangers which contain cations or anions as counterions are called cation exchangers or anion exchangers, respectively. The usual matrix is polystyrene cross linked for structural stability with 3 to 8 percent of divinylbenzene (3-8 % DVB) [23, 24].

Depending on the type of functional groups of exchanging certain ions, the ion exchangers with strongly acidic e.g., sulphonate $-SO_3H$, weakly acidic e.g., carboxylate -COOH, strongly basic e.g., quaternary ammonium $-N^+R_3$ and weakly basic e.g., tertiary and secondary amine $-N^+R_2H$ and $-N^+RH_2$ should be mentioned. The strong acidic cation exchangers are well dissociated over a wide pH range and thus reaching its maximum sorption capacity. On the other hand, weak acidic cation exchangers containing, for example, carboxylic functional groups reach the maximum sorption capacity at pH > 7.0 as presented in Figure 2.3 [25].

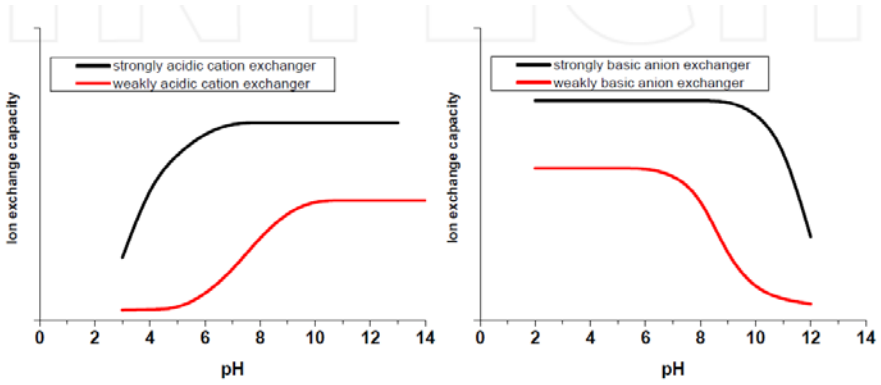

Figure 2.3 The sorption capacity of ion exchangers depending on pH [25]

There are also amphoteric exchangers, which depending on the pH of the solution may exchange either cations or anions. More recently these ion exchangers are called bipolar electrolyte exchange resins (BEE) or zwitter-ionic ion exchangers [26].

2.2.1 Cation exchangers with the sulphonic functional groups

It is well known that the affinity of sulphonic acid resins for cations varies with the ionic size and charge of the cation. The affinity towards cation increases with the increasing cation charge:

$$Na^{+} < Ca^{2+} < Al^{3+} < Th^{4+},$$

and in the case of different cations with the same charge the affinity increases with the increasing atomic number:

$$Li^{+} < H^{+} < Na^{+} < NH_4^{+} < K^{+} < Rb^{+} < Cs^{+} < Ag^{+} < Tl^{+}$$

$$Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$$

$$Al^{3+} < Fe^{3+}.$$

Generally, the affinity is greater for large ions with high valency [25].

2.2.2 Cation exchangers with the carboxylic functional groups

Cation exchangers with the carboxylic functional groups show the opposite the affinity series for alkali and alkaline earth metal ions. Noteworthy is the fact that the cations exhibit a particularly high affinity for H+. The affinity of this type of cation is therefore as follows [25]:

$$H^{+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Li^{+} > Na^{+} > K^{+} > Rb^{+} > Cs^{+}.$$

2.2.3 Anion exchangers with the quaternary ammonium functional groups

The charge of the anion affects its affinity for the anion exchanger in a similar way as for the cation exchangers [25]:

$$\text{Citrate} > \text{Tartrate} > PO_4^{3-} > AsO_4^{3-} > ClO_4^{-} > SCN^{-} > I^{-} > S_2O_3^{2-} > WO_4^{2-} > MoO_4^{2-} > CrO_4^{2-} > C_2O_4^{2-} > SO_4^{2-} > SO_3^{2-} > HSO_4^{-} > HPO_4^{2-} > NO_3^{-} > Br^{-} > NO_2^{-} > CN^{-} > Cl^{-} > HCO_3^{-} > H_2PO^{4-} > CH3COO^{-} > IO_3^{-} > HCOO^{-} > BrO_3^{-} > ClO_3^{-} > F^{-} > OH^{-}.$$

2.2.4 Anion exchangers with the tertiary and secondary amine functional groups

Only with the exception of the OH^- ion, the affinity of the anion exchangers with the tertiary and secondary functional groups is approximately the same as in the case of anion exchangers with the quaternary ammonium functional groups. These medium and weakly basic anion exchangers show very high affinity for OH^- ions.

Anion exchange materials are classified as either weak base or strong base depending on the type of exchange group. These are two general classes of strong base anion exchangers e.g. types 1 and 2 depending on chemical nature. The synthesis of the weak base anion exchangers with the tertiary amine groups is usually provided by the chloromethylation of PS-DVB followed by the amination by secondary amine [27]. Weak base resins act as acid adsorbers, efficiently removing strong acids such as sulphuric and hydrochloric ones. They are used in the systems where strong acids predominate, where silica reduction is not required, and where carbon dioxide is removed in degasifiers. The affinities of various functional groups following the order: primary > secondary > tertiary > quaternary. Therefore among the factors affecting the sorption equilibrium the most important are: first of all nature of functional groups and the concentration of the solution [28]. It should be also mentioned that obtaining resins with the primary amine functional groups is difficult by chemical reactions on polystyrene-divinylbenzene copolymers.

2.3 Functional Polymers

Since the first generation of ion-exchange resins and membranes, the development of functional polymer chemistry and technology has made remarkable progress in recent years. For example, studies related to the preparation and design of several enzymes and nucleic acid models have advanced dramatically, and the development of the technology necessary to use these polymers is of current interest.

Functional polymers, in a broad sense, include a variety of polymeric materials and a number of engineering plastics. These polymer systems often exhibit more specific and better properties if processed as polymer aggregates. For example, organic polymers with polyconjugated double bonds consisting of special structures are known as synthetic metals, which show substantially high electron conductivity in a

fiber or film form. On the other hand, ceramic materials with new properties, such as elasticity, have only recently prepared by organic synthetic techniques.

Recently, microporous polymeric materials as well as microcapsules have become of interest in a variety of industrial fields, not only in the general chemical industry, but also in the pharmaceutical, biomedical and electronics industries. For example, fluorine-containing resins are important, particularly, as a safe and durable anti-thrombogenic biomaterial. Microporous membranes made of vinyl polymers are being applied as separators or filters to concentrate oxygen from air and to manufacture ultrahigh grades of water for the semiconductor industry. Other types of microporous vinyl polymers are being used as highly hydrophilic materials in the fields of cosmetics and environmental hygiene.

The science and technology required for the preparation of microcapsules from different natural and synthetic polymeric materials has made rapid progress. They are being used in various fields for their ability to solidify liquids; to isolate reactive compounds; to remove color, odor, and toxicity; as well as to regulate and control the release of included compounds. The immobilization of enzymes and the development of polymeric drugs are also playing an important role.

In addition, highly water-absorbing and oil-absorbing resins are of interest. These have developed rapidly in recent years by unique grafting and crosslinking of hydrophilic polymers. Transparent polymeric materials with optical functions are also noteworthy. Some are biocompatible, such as poly (2-hydroxethyl methacrylate), which serves as a material for soft contact lenses. Plastic optical fibers are also widely used as substitutes for glass and quartz devices in various fields of technology, especially the biomedical and communication sciences.

The chemistry of so-called electronic functional polymers, in a narrow sense, has developed into a very exciting subject, particularly in the last 10 years. Some of the most attractive materials in this field are the photosensitive and photo responsive polymers. By using these phenomena, specifically designed polymers undergo reversible crosslinking reactions to become insoluble or soluble. A variety of both negative and positive types of photoresists are being produced. They are initially used in printing, paint, and color industries. The technology to exploit deep ultraviolet (UV) radiation resist with reversible functionality will be one of the most

important developments in this industry in the near future. Other subjects of interest in this field, which are under development, are the electronic or X-Ray sensitive resists, as well as the design of more functional photo memory materials.

In connection with biomedical polymers, the chemistry of the polymeric drugs is under continuous advancement. The most effective anti-carcinogenic reagent is now targeted by the design of specifically functionalized polymers. The functional polymeric composites are also particularly attractive as implant materials [29].

2.3.1 Properties of functional polymers

There are a number of considerations in the choice of the functional polymers to be used in a specific application functionalized polymer must possess a structure which permits adequate of reagent in the reactive sites. This depends on the extent of swelling compatibility the effective pore size, pore volume (porosity) and the chemical, thermal and mechanical stability of the resins under the conditions of a particular chemical reaction on reaction sequence. This in turn depends on the degree of the crosslinking of the resin and the conditions employed during its preparation.

The use of cross-linked polymers in chemical applications is associated with some advantages, such as the following.

1) Since they are in soluble in our solvents, they offer the greatest is of processing.
2) They can be prepared in the form of spherical beads and can be separated from low molecular weight cont0amined by simple filtration and washing with very use solvents.
3) Polymer beads with very low degrees of crosslinking swell extensively, exposing their inner reactive groups to the soluble reagents.
4) More highly cross-linked resins may be prepared with very porose structures which allow solvents and reagents to penetrate inside of the beads to contact reactive groups.

The following is a classification of the types of cross-linked polymers which are most frequently encouraged with enhanced properties.

a. Microporose pore gel-type resins

These types are generally prepared by suspension polymerization using a mixture of vinyl monomer and small amounts (less tan %10; in most cases less than % 0.5 - % 2) of a crosslinking agent containing no additional solvent.

Swellable polymers are found to offer advantage over non-swellable polymers of particular interest is their lower fragility, lower sensitivity.

b. Macropores and macro reticular resins

The mechanical requirements in industrial applications force the use of higher crosslinking densities for preparing density with enhanced properties. Macropores and macro reticular resins are also prepared by suspension polymerization using higher amounts of crosslinking agents but with the inclusion of an inert solvent as diluents for the monomer phase.

Macroreticular resin is non-swelling and a macro pores a rigid material with a high crosslinking it retains its overall shapes and volume when the precipitate is removed.

To sudden shock and their potential to achieve a higher leading capacity during functionalization however, a degree in crosslinking density will increase swelling but will also result in soft gels which generally have low mechanical stability and readily in fragment even under careful handling. Gels with lower density of crosslinking are difficult to filter and under sever conditions can degrade to produce soluble linear fragments in addition gel type resins that are likely cross-linked may suffer considerable mechanical damage as a result of rubit and extreme change in the nature of the solvating media and cannot be subjected to study and high pressures. Macropores resins with less than % 1 crosslinking generally have low mechanical stability while macropores resins with more than % 8 crosslinking are mechanically stable but unfortunately give rise to acute [30].

2.3.2 Cross-linked polymers

Physiosorption, *grafting*, and *crosslinking* are the techniques by which the association of monomers and polymers is described. The term physiosorption signifies that it is related to physical attractive forces. The process is a reversible one and is achieved by the end functionalized polymers on to the solid surface or self - assembly of polymeric surfactants, where *grafting* can be described as the covalent attachment process and irreversible. Grafting can be accomplished by either “grafting

to" or "grafting from" approaches. In "grafting to" approaches, functionalized monomers react with the backbone polymer to form the grafted one. On the other hand, "grafting from" is achieved by treating a substrate with some method to generate immobilized initiators followed by polymerization. High grafting density polymer also can be accomplished using this technique. The schematic presentation of all the processes is depicted in Figure 2.4 A. The *crosslinking* is the association of polymers through a chemical bond. In most cases, the crosslinking is irreversible. It may be intra - and intermolecular (Figure 2.4 B) [31].

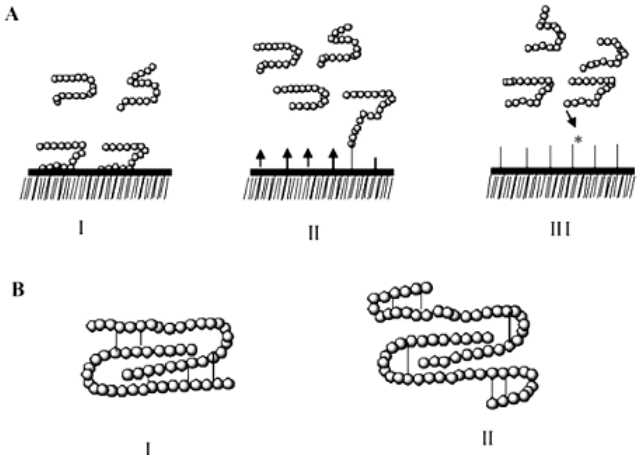

Figure 2.4 ***A.*** Schematic diagram of (I) physiosorption, (II) grafting to, (III) grafting from. ***B.*** Schematic diagram of (I) intermolecular crosslinking and (II) intramolecular crosslinking [32].

2.4 Polymeric Sorbents in Metal Removal

Metal ions are non-biodegradable in nature, and their intakes at a certain level are toxic. Electrochemical methods, chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation-flocculation and flotation are methods that have been used to treat heavy metal waste waters [32-39]. Conventional methods have limited success in the extraction of trace quantities [40]. Since the target species are usually in low concentration and in complex mixtures, it is necessary to remove toxic metals by using more efficient polymeric sorbents.

A polymeric sorbent essentially consists of two components: the functional group and the polymeric matrix or the support; the properties of both components determine the features and the applications of the respective material. While chelating group usually determines the selectivity of the sorbent which depends on the nature of the functional group and/or donor atom able to form complexes with

metal ions, polymeric matrix determines other analytical properties, namely the capacity, kinetic features, mechanical and chemical strength and regeneration [41].

2.4.1 Physico - Chemical properties of polymeric sorbents

Functional group determines the sorption capacity of sorbents which depends on the surface area of the support, the ionic strength and pH of the solution. The property of the sorbent to react with metallic ions under certain favorable conditions is determined by the nature of functional groups and/or donor atom (O, N, S). Selectivity of suitable specific functional groups fixed into the polymeric matrix has been explained on the basis of the concept of strong and weak acids and bases [42].

Functional groups in the sorbents usually act as bases: oxygen containing functional groups have strong, sulphur-containing groups have weak and nitrogen-containing groups have an intermediate character. Equilibriums for the complex formation of chelating sorbents towards some metal ions have been studied by several authors [43-46].

Kinetic characteristics of the sorbent depend on the nature and properties of polymeric matrix. Cross-linked polymers are preferred as polymeric support for several reasons. Firstly, cross-linked polymers have high chemical stability, mechanical strength and adjustable chemical surface. Since they are in soluble in solvents, they offer a great processing. In addition, they can be prepared in the form of spherical beads and can be separated from low molecular weight contaminants by simple filtration and washing with very use solvents. Furthermore, polymer beads with very low degrees of crosslinking swell extensively, exposing their inner reactive groups to the soluble reagents. More highly cross-linked resins may be prepared with very porous structures which allow solvents and reagents to penetrate inside of the beads to contact reactive groups [47].

Measurement of the sorption rate under the conditions of diffusion through the particle as the rate-determining process proves the effect of the functional group concentration and of the sorbent structure on its kinetic properties. The time of establishing the sorption equilibrium varies from a few minutes to hours. Polystyrene-based sorbents exhibit poor kinetic properties because of the hydrophobic nature of the matrix. The sorbents with the best kinetic characteristics

are those based on typically hydrophilic matrices, such as cellulose or macro-porous methacrylate copolymers [48-51].

2.4.2 Complexation of polymeric ligand and metal ion

The analytical applications of chelating polymer depend on many factors. Normally a metal ion exists in water as a hydrated ion or as a complex species in association with various anions, with little or no tendency to transfer to a chelating polymer. To convert a metal ion into an extractable species its charge must be neutralized and some or all of its water of hydration must be replaced.

The nature of the metal species is therefore of fundamental importance in extraction systems. Most significant is the nature of the functional group and and/or donor atom capable of forming complexes with metal ions in solution and it is logical to classify chelating polymers on that basis.

This method of classification is not meant to imply that these systems are mutually exclusive. Indeed some polymers can belong to more than one class, depending on experimental conditions [52]. Among the many ligands [53] introduced 8-acryloyloxyquinoline is one of the recent origin.

This kind of polymer-metal complexes are prepared by the chemical reaction of a polymer, containing ligands with metal ions.

Generally, the reaction of a polymeric ligand with a metal ion or a stable metal complex, in which one coordination site remains vacant, results in different structures that can be grouped into pendant and inter/intra-molecular bridge polymer-metal complexes [54].

2.4.3 Inter/intra-molecular bridged polymer-metal complexes

When a polymer ligand is mixed directly with metal ion, which generally has four six coordinate bonding sites, the polymer-metal complex formed may be of the intra-polymer chelate type or inter polymer chelate type as shown in Figure 2.5.

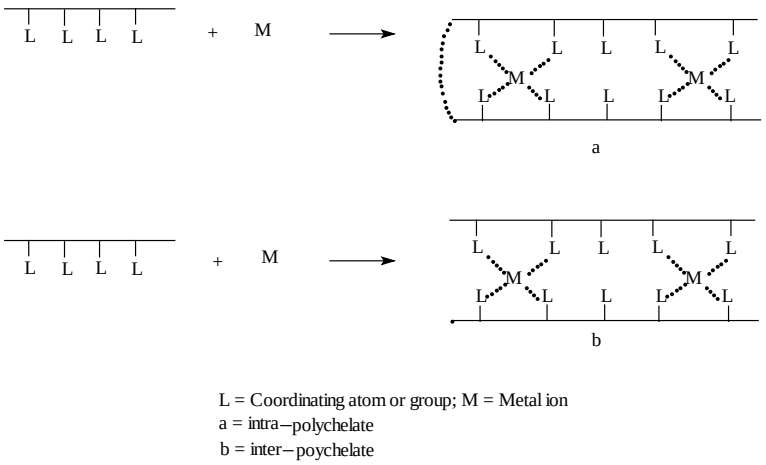

Figure 2.5 Inter/intra molecular bridged polymer-metal complexes

The coordination structure in this type of polymer-metal complex is not clear and it is often difficult to distinguish between inter/intra-molecular bindings. Thus it is not easy to elucidate the polymer effect in studying the characteristics of the polymer-metal complexes. Intra-polymer metal complex is sometimes soluble, while inter-polymer metal complex results precipitation of the linear polymer-metal complexes as exemplified by poly (acrylic acid)-Cu (II) complex [55].

2.4.4 Sorbents depending on their backbone

Chelating polymers can be divided into two classes depending on the origin of their backbone: graft adsorbents and graft biosorbants.

2.4.4.1 Graft adsorbents

Graft adsorbents are a class of chelating polymers that have a modified backbone of synthetic polymers containing immobilized functional groups. These adsorbents have the flexibility of being prepared with various combinations of functional - group - containing grafts (e.g., polyamines, polyacrylonitrile, polyacrylamides, and polyacrylic acid) and polymer substrates such as polyethylene (PE), polypropylene (PP), and PTFE, thus opening a broad spectrum of prospects for tailor - made applications such as the removal of toxic heavy metals and recovery of precious metals. The adsorption mechanisms in these polymers have generally been attributed to the formation of complexes between the functional groups on the adsorbents and the metal ions to be removed [29].

2.4.4.2 Grafted and cross-linked biosorbents

Grafted and cross-linked biosorbents are a class of chelating polymers that have a modified backbone of biopolymers (polysaccharides) such as chitosan, alginate, starch, and cellulose. These biosorbents are much more selective yet cheaper than traditional ion exchange resins, although their native form shows inferior biosorbance performances caused the instability of physical and chemical properties. Therefore, modification of these polysaccharides has been explored as a way of combining their best attributes with those of synthetic graft polymers. Several functional groups such as amino, phosphate, amido, sulfonate and carboxyl, and hydroxyl groups can be grafted onto the polysaccharides to give them additional ionic characters with their stability further enhanced by crosslinking.

The bio sorption mechanism in these grafted and cross-linked materials is a complex process involving (i) ion exchange, (ii) chelation, (iii) complexation, and (iv) adsorption by physical forces such as H - bonding, entrapment in inter and intrafi brilliar capillaries, and spaces of the structural polysaccharides network as a result of the concentration gradient and diffusion through the sorbent.

Particularly, chitosan - based biosorbents are efficient selective materials that have been frequently used in various separation applications including removal of heavy metals and dyes. For example, beads obtained by the casting of cross-linked and grafted chitosan have high porosity and large surface areas, high stability in acidic media, and are most suitable for industrial applications. Other biopolymers such as starch and cyclodextrins have been also proposed as low - cost biosorbents. The recent developments in the synthesis of biosorbents obtained from modified polysaccharides (starch, cyclodextrin, chitin, and chitosan) were reviewed by Cirni [29].

2.4.5 Sorbents for mercury removal depending on their functional group

Sulfur and amide are the two common ligand types, which are being used currently in the design of polymer sorbents for binding mercuric ions selectively. Mercury, in its various forms, has a great affinity for certain atoms. Sulfur is one of the most important atoms that mercurial have a great attraction to. The mercury atom or molecule will tend to bind with any molecule present that has sulfur or a sulfur

hydrogen combination in its structure. Thus sulfur containing ligands has received much recent attention, in part due to this great affinity. Nitrogen is the other important atom that has a great affinity for mercury ion. Especially amide ligands tend to complex with mercury ion. Amide compounds readily react with mercuric ions under ordinary conditions to give mono- or diamidomercury compounds. The mercury–amide linkage is believed to be covalent rather coordinative [56]. In the past decade, there are several studies were conducted on removal of Hg (II) ions from aqueous media by polymers carrying pendant sulfur and nitrogen containing ligands. Senkal et al. synthesized poly (acrylamide) grafted poly (styrene) (Figure 2.6) and removed mercury ions with 5.75 mmol/g sorbent removing capacity [57].

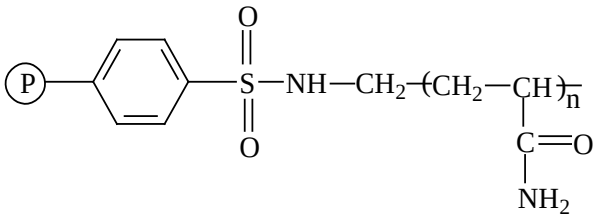

Figure 2.6 Poly (acrylamide) grafted poly (styrene) [58].

Cross-linked Poly (glycidyl methacrylate) (PGMA) based resin with acetamide functional group (Figure 2.7) were demonstrated to be efficient in the removal of mercury by Senkal et al. in 2006. The mercury sorption capacity of the resin was found as 2.2 mmol/g resin in this study [58].

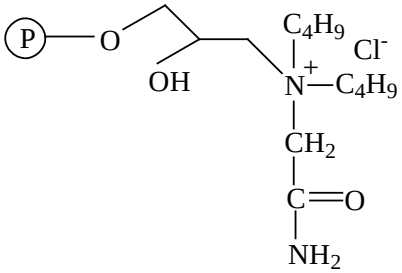

Figure 2.7 Crosslinked PGMA based resin with acetamide functional group [55].

Cellulose based sorbents have been studied by several research groups all around the world because of the excellent properties that cellulose serves. Poly (acrylamide) grafted onto cellulose was synthesized by Bicak et al. (Figure 2.8) has been demonstrated to be a very efficient selective sorbent for removal of Hg (II) from aqueous solutions [59].

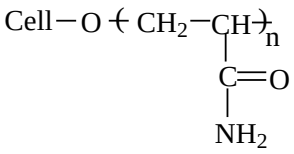

Figure 2.8 Poly (acrylamide) grafted cellulose [59].

A new polymeric resin with thiol pendant functions has been prepared for the extraction of mercuric ions. The thiol containing sulfonamide based resin with 3.5 mmol/g total nitrogen content is able to selectively sorb mercury from aqueous solutions. The mercury sorption capacity of the resin is around 1.70 mmol/g under non-buffered conditions [60].

2.5 Adsorption Isotherms Models

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH [61, 62]. Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration [63, 64].

Its physicochemical parameters together with the underlying thermodynamic assumptions provide an insight into the adsorption mechanism, surface properties as well as the degree of affinity of the adsorbents [65].

Over the years, a wide variety of equilibrium isotherm models (Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich– Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm), have been formulated in terms of three fundamental approaches [66]. In this study three models, which are Langmuir, Freundlich and Dubinin–Radushkevich, were examined.

Table 2.2 List of adsorption isotherms models

Isotherm	Nonlinear Form	Linear Form	Plot
Langmuir	$q_e = \frac{Q_0 b C_e}{1 + bC_e}$	$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0 C_E}$	$\frac{1}{q_e}\ vs\ \frac{1}{C_e}$
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n}\log C_e$	$\log q_e\ vs\ \log C_e$
Dubinin–Radushkevich	$q_e = (q_s)\exp(-k_{ad}\varepsilon^2)$	$\ln(q_e) = \ln(q_s) - k_{ad}\varepsilon^2$	$\ln(q_e)\ vs\ \varepsilon^2$

2.5.1 Langmuir isotherm model

Langmuir adsorption isotherm, originally developed to describe gas–solid-phase adsorption onto activated carbon, has traditionally been used to quantify and contrast the performance of different bio-sorbents [67]. In its formulation, this empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites [68]. In its derivation, Langmuir isotherm refers to homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate) [69], with no transmigration of the adsorbate in the plane of the surface [70]. Separation factor (R_L) can be represented as:

$$R_L = \frac{1}{1 + K_L C_0} \quad \textbf{(2.1)}$$

where K_L (L/mg) refers to the Langmuir constant and C_0 is denoted to the adsorbate initial concentration (mg/L). In this context, lower R_L value reflects that adsorption is more favorable. In a deeper explanation, R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

2.5.2 Freundlich isotherm model

Freundlich isotherm [71] is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform

distribution of adsorption heat and affinities over the heterogeneous surface [72]. In this perspective, the amount adsorbed is the summation of adsorption on all sites (each having bond energy), with the stronger binding sites are occupied first, until adsorption energy are exponentially decreased upon the completion of adsorption process [73].

2.5.3 Dubinin–Radushkevich isotherm model

Dubinin–Radushkevich isotherm [74], is an empirical model initially conceived for the adsorption of subcritical vapors onto micro pore solids following a pore filling mechanism. It is generally applied to express the adsorption mechanism [75] with a Gaussian energy distribution onto a heterogeneous surface [76].

The approach was usually applied to distinguish the physical and chemical adsorption of metal ions [77], with its mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be computed by the relationship [78]:

$$E = \left[\frac{1}{\sqrt{2B_{DR}}}\right] \quad \textbf{(2.2)}$$

where B_{DR} is denoted as the isotherm constant. Meanwhile, the parameter ε can be correlated as:

$$\varepsilon = RTln\left[1 + \frac{1}{C_e}\right] \quad \textbf{(2.3)}$$

where R, T and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively [79].

3. EXPERIMENTAL

3.1 Materials and Instruments

3.1.1 Materials

Styrene (Fluka), Divinyl benzene (Aldrich) 55% of which is a mixture of meta and para isomers), Chloroacetic acid (E.Merck), Tris(2-aminoethyl) amine (Aldrich), Diphenylcarbazide (E-Merck), Mercury(II) chloride (E-Merck) , Iron(III) chloride (E-Merck), Magnesium sulphate (E-Merck), Cadmium nitrate (E-Merck), HCl (E-Merck), and all the other chemicals used were analytical grade commercial products.

3.1.2 Instruments

UV-vis spectrophotometer (Perkin Elmer, Lamda 25) and Thermo FT-IR (with ATR).

3.2 Preparation of The Polymeric Sorbent

3.2.1 Crosslinked Poly (styrene-divinyl benzene) (PS) beads

Beads were prepared by the suspension polymerization of a mixtured styrene (54 mL, 0.48 mol) and DVB (55 % grade, 10 mL, 0.038 mol) in toluene (60 mL), using gum-Arabic as stabilizer, according to a previously described procedure [80]. The beads were sieved and the 420-590 μm size fractions were used for further reactions.

3.2.2 Chlorosulfonation of the PS-DVB beads

The beaded polymer was chlorosulfonated using chlorosulfonic acid as described in the literature [81]. In this study, 10 g PS beads was interacted with the excess of chlorosulfonic acid (50 mL, 0.76 mol) at 0 ^{0}C for 20 min and at room temperature for 24 h. Chlorosulfonated resin was filtered under vacuum and was washed with excess of cold water, acetone and ether respectively. The degree of chlorosulfonation was determined by analysis of the liberation of chloride ions. For these purpose, a polymer (0.2 g) sample was added to 10 % NaOH (20 mL) and boiled for 4h. After

filtration and neutralization with HNO_3 (5 M), the chlorine content was determined by the mercuric-thiocyanate method [81]. This gave a final chlorosulfonation degree of 3.50 mmol.g^{-1}.

3.3 Preparation of Sulfonamide Based Resin (resin 1)

Chlorosulfonated resin (9.80 g) was added portion wise to a stirred of tris (2-aminoethyl) amine (10 mL, 47.58 mmol) in 50 mL of 2-methyl pyrrolidone at 0^0C and at 60 ^{0}C for 5 h. The mixture was shaken with a continuous shaker for at room temperature. The reaction content was poured into water (1L), filtered and washed with excess water and ethanol respectively. The resin dried under vacuum at room temperature for 24 h. The yield was 15.0 g.

The sulfonamide content was determined according to the literature [82] and found to be 3.00 mmol.g^{-1}.

3.4 Amidation of The Resin (resin 2)

4 g of the resin 1 was added to 50 mL of the chloroform. The reaction mixture was cooled to 0 ^{0}C by using ice bath. Excess of the acetyl chloride (5 mL in 20 mL chloroform) was added drop wise to the mixture in the presence of trimethylamine as an acid scavenger by using dropping funnel at 0 ^{0}C for 30 minute. The reaction was continued at 0 ^{0}C for 1 h and at room temperature for 24 h. Then, reaction content was filtered and washed with excess of chloroform, acetone, water and ethanol, respectively. The product was dried under vacuum at room temperature for 24 h. The yield was found as 5.20 g.

3.5 Mercury Uptake Experiments

In this thesis, $HgCl_2$ was used as mercury salt. Hg (II) sorption experiments of the resin 2 were carried out at different mercury concentrations and pH.

3.5.1 Determination of the mercury loading capacity of the resin

The mercury sorption experiments were performed in non-buffered conditions. In these experiments, 0.1 g of the resin was wet with distilled water (1.5 mL) and was added to 10 mL of Hg (II) solutions. The mixture was shaken on a continuous shaker

for 24 h and filtered. 1 mL of the supernatant solution was transferred to a volumetric flask and diluted to 100 mL with water.

The Hg (II) concentrations were determined colorimetrically using diphenyl-carbazide [84].

3.5.2 Determination of the mercury loading capacity of the resin depending on pH

0.05 M $HgCl_2$ was dissolved in different pH (2, 4, 5, 6) and 0.1 g of the resin was put into the 10 mL of $HgCl_2$ solutions and was stirred at room temperature for 24 h. Then, the mixture was filtered. Mercury loading capacities of the resin were found described above.

3.5.3 Sorption tests for foreign ions

In order to examine the selectivity of Hg (II) binding, sorption capacity of Cd (II), Mg (II), Pb (II) and Fe (III) were determined. For this purpose, 0.1 g of the resin was interacted with 0.05 M metal salts. The mixtures were stirred for 24 hours and then filtered. Analyses of the residual metal contents of the supernatant solutions were performed by a complexometric titration method using EDTA solution (0.05 M).

3.6 Kinetics of Mercury Uptake

In order to estimate efficiency of the Resin 2 for trace mercury batch kinetic experiment was performed using high diluted $HgCl_2$ ($1x10^{-4}$ M $HgCl_2$) solutions. For this purpose 0.30 g of sorbent was wetted with 1 mL of distilled water and added to 90 mL $HgCl_2$. The mixture was stirred magnetic stirring bar and aliquots of the solution (3 mL) were taken at appropriate time intervals for analysis of the residual Hg (II) contents by the method as mentioned above.

Kinetic and adsorption models were applied to the resin.

4. RESULTS AND DISCUSSION

4.1 Preparation of Chlorosulfonated Polystyrene resin (CSPS)

Crosslinked polystyrene – DVB copolymer was prepared by using suspension polymerization method. The polymer was chlorosulfonated by using excess of chlorosulfonic acid at room temperature for 24 h (Figure 4.1).

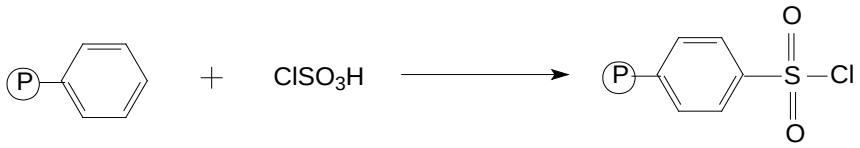

Figure 4.1 Chlorosulfonation of the cross-linked polystyrene

Chloride analysis of the product in the first step (3.50 mmol.g^{-1}) revealed a degree of chlorosulfonation of ~ 61 %.

4.2 Reaction with CSPS Resin and Tris (2-aminoethyl) Amine (Resin-1)

Crosslinked sulfonamide based resin was prepared starting from reaction with chlorosulfonated polystyrene and excess of tris (2-aminoethyl) amine (Figure 4.2).

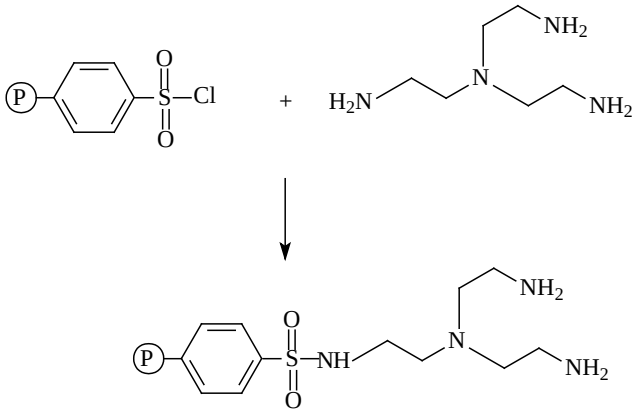

Figure 4.2 Preparation of the Resin 1

The resin 1 was characterized by detection of sulfonamide content and was found as about 3.0 mmol.g^{-1}.

4.3 Reaction of Resin 1 with Acetyl Chloride (Resin 2)

Reaction of resin 1 with excess acetyl chloride gives amide-sulfonamide resin (resin 2) (Figure 4.3).

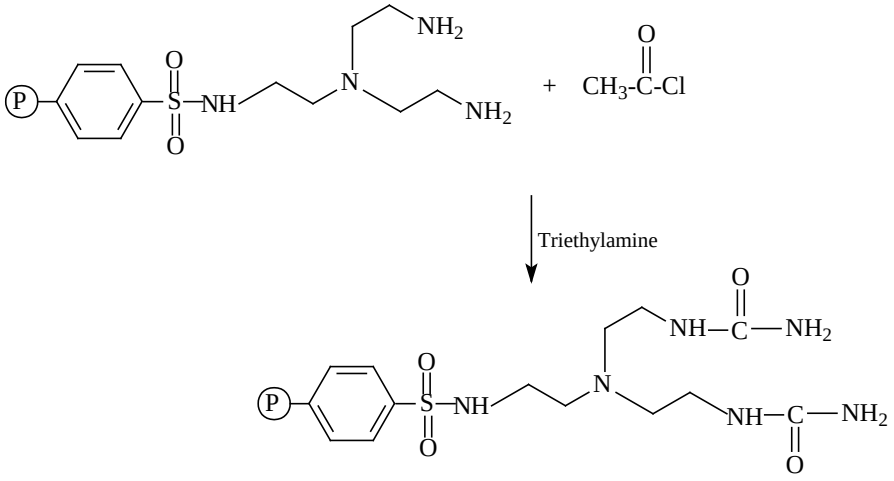

Figure 4.3 Preparation of Resin 2

Spectroscopic characterization of the resins were performed by FT-IR. In the sulfamidation products for Resin 1 and Resin 2, S=O stretching vibrations of sulfonamide group appear at about 1315 and 1147 cm^{-1}. In addition, the sharp peak at about 1685 cm^{-1} corresponds to C=O stretching vibration of the amide group in the Resin 2. N-H stretch peak at 3060 cm^{-1} belong to primary amide group was observed in (Figure 4.1b).

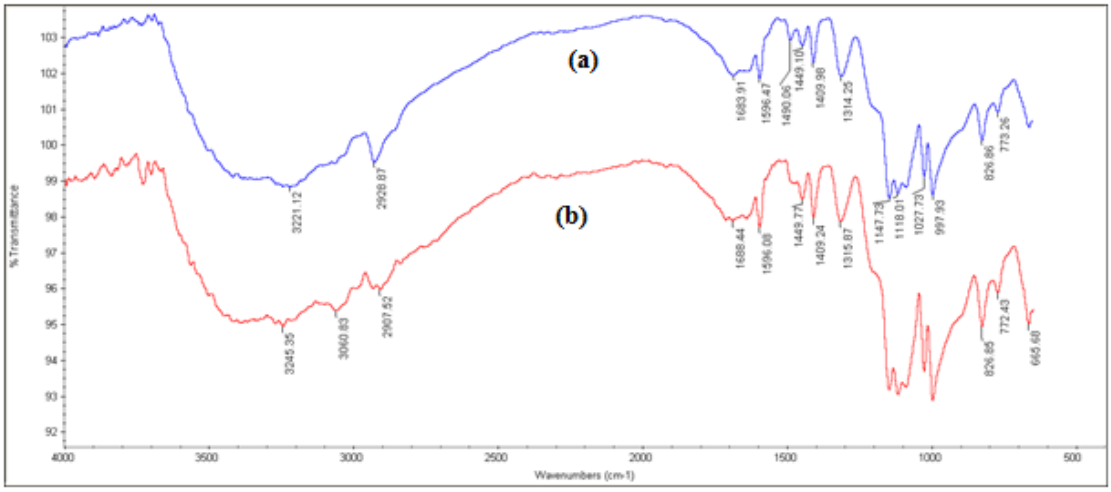

Figure 4.4 FT-IR spectra of the Resin 1 (a) and Resin 2 (b).

4.4 Mercury Uptake of the Resin 2

The Amide containing polymeric sorbent was an efficient sorbent to remove mercury. On the basis of the basic reaction of the mercuric ions with amide groups, this yielded covalent mercury–amide linkages [56]. The mercury binding of the polymer can be depicted as shown in Figure 4.5.

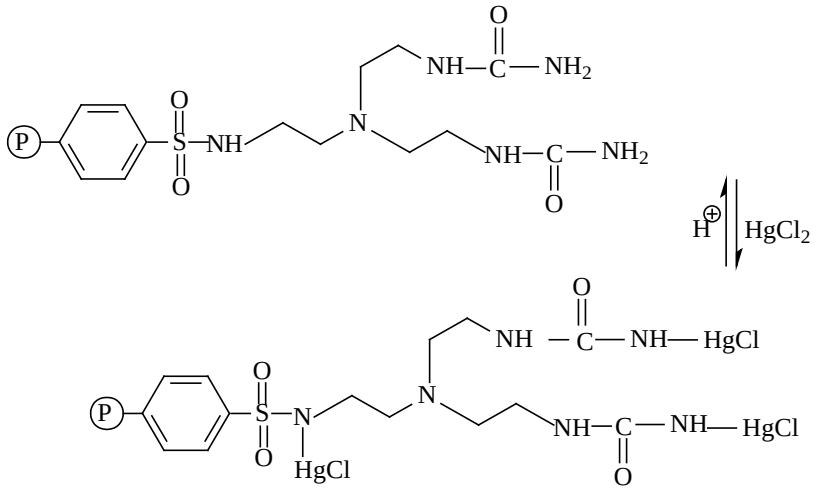

Figure 4.5 Mercury uptake of Resin 2.

The mercury sorption capacities of the resins were determined by mixing weighed amount of polymer sample (0.1 g) with 10 mL aqueous Hg (II) solutions with different concentrations (0.0625-0.1 M).

Capacities of the Resin 2 were given in the Table 4.1. In these experiments, buffer solutions were not used and pH of the mercury solutions in water was found about 3.5.

Table 4.1 Mercury sorption capacities of the Resin 2

Concentration [$HgCl_2$], M	Capacity (mmol Hg/g resin)
0.10000	1.90
0.05000	1.20
0.02500	0.65
0.01250	0.30
0.00625	0.18

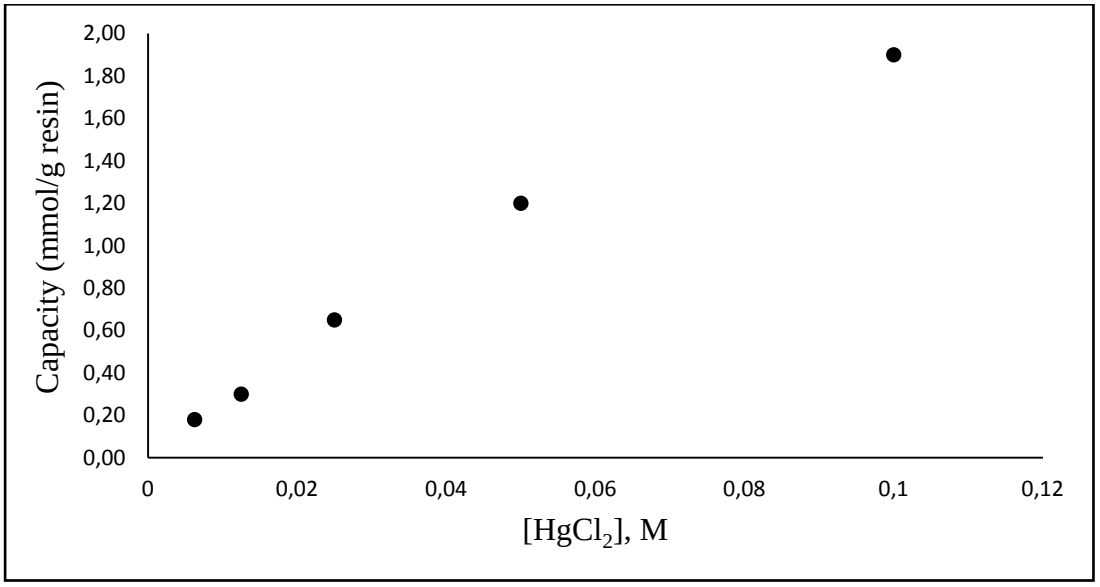

Figure 4.6 Concentration of $HgCl_2$ – Capacity of resin 2 plot

According to the Table 4.1 and Figure 4.6, mercury loading capacity of the resin 2 depending on the initial mercury concentration and loading capacity of the resin 2 increases with increasing of the initial concentration.

Mercury adsorption experiments also were carried out at various pH's in either phosphate buffer (pH=6) and acetate buffer (pH=4, 5). 0.01 M HCl acid solution was used for pH=2. The results are given in the Table 4.2. According to the results obtained mercury adsorption capacity of the resin 2 increased by increasing pH. Because of proton releasing during the binding, pH values closer to neutral condition are much favorable.

Table 4.2 Changing capacity depend on pH

pH	Capacity (mmol / g resin)
2	**0.926**
4	**2.083**
5	**3.12**
6	**4.33**

The loading experiments indicated a mercury capacity of about 1.9 mmol/g under non-buffered conditions and 4.33 mmol/g. at pH 6.

Other metal ions sorption capacities of the Resin-2 between1.0-2.20 mmol.g-1 were observed (Table 4.3). The resin 2 has tertiary amine group therefore other metal ions can bind the resin 2 but mercury loading capacity of the resin 2 is higher than the other cations.

Table 4.3 Metal uptake characteristics of the Resin 2.

Metal ion	Initial concentration (M)	Resin capacity (mmol / g resin)
Hg(II)	0.05	4.33
Cd(II)	0.05	2.20
Mg(II)	0.05	2.15
Pb(II)	0.05	2.38
Fe(III)	0.05	1.00

4.5 Kinetics of the Mercury Sorption

To examine the efficiency of the Resin 2 for trace quantities, kinetic experiments were investigated with extremely diluted $HgCl_2$ solutions (1.0×10^{-4} M).

The kinetics of the mercury sorption depends on many factors, such as stirring rate and pH of the solution. To obtain information about kinetic profiles of the mercury sorption, we performed experiments by the batch method with low mercury concentrations under non-buffered conditions. The concentration–time and capacity-time plots in Figure 4.3 and 4.4 show that within about 1 hour of contact time, the Hg(II) concentration falls to zero and the capacity is increasing with time.

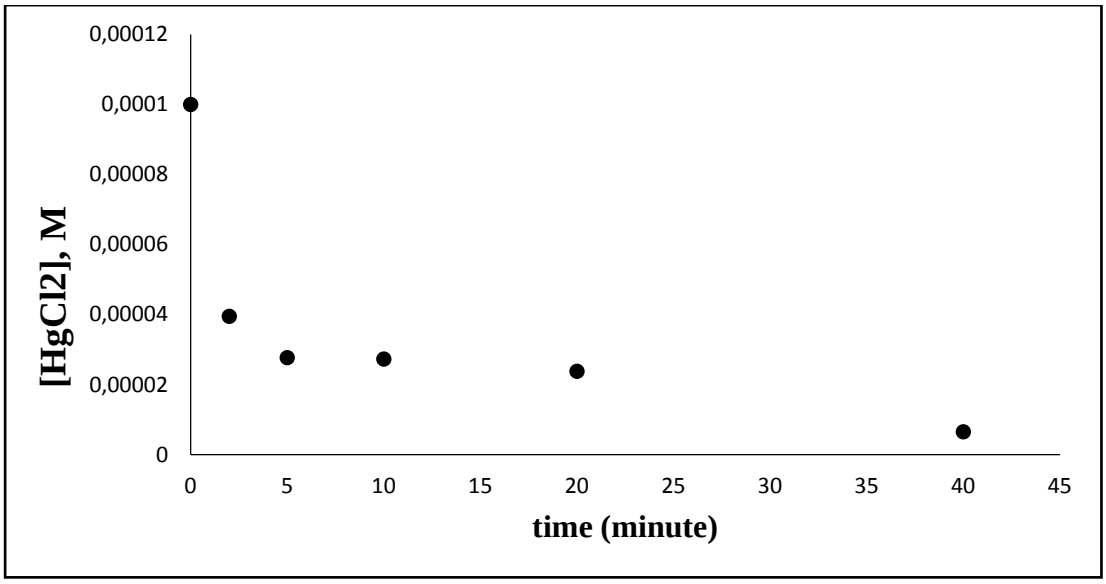

Figure 4.7 Hg (II) adsorption kinetics of the Resin 2

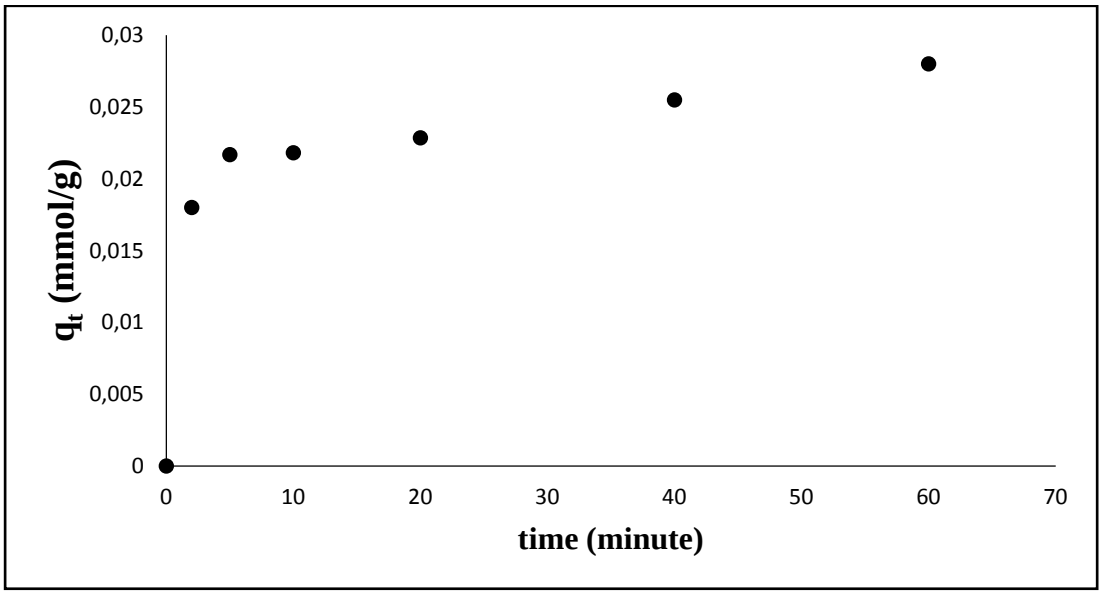

Figure 4.8 Capacity of resin 2

Adsorption dynamics is useful to describe the rate of solute adsorption, which controls the residence time of uptake of the adsorbate at the solid–solution interface. Three kinetic models were used to analyze adsorption kinetics at different initial mercury concentrations: pseudo-first-order, pseudo-second-order, and intra-particle diffusion models [84].

The rate constant of adsorption was studied with the help of the pseudo-first-order rate expression of Lagergren model, the pseudo-second-order kinetic rate expression of [85-87] and Intra-particle Diffusion Model.

The pseudo-first-order equation assumes that the adsorption rate decreases linearly as the adsorption capacity increases, which is suitable especially for low concentrations [87]. A linear form of this model is:

$$\ln(q_e - q_t) = lnq_e - \left(\frac{k_1}{2.303}\right)t \qquad \textbf{(4.1)}$$

Where q_t and k_1 are the amount of dye adsorbed at time t (mmol/g) and the equilibrium rate constant of pseudo-first-order kinetics (1/ min), respectively. The linear fitting of log (q_e-q_t) with the contact time (t) can be approximated as pseudo-first-order kinetics (Figure 4.5). The low correlation coefficient value obtained for the pseudo-first-order model indicated that adsorption was not occurred exclusively onto one site per ion.

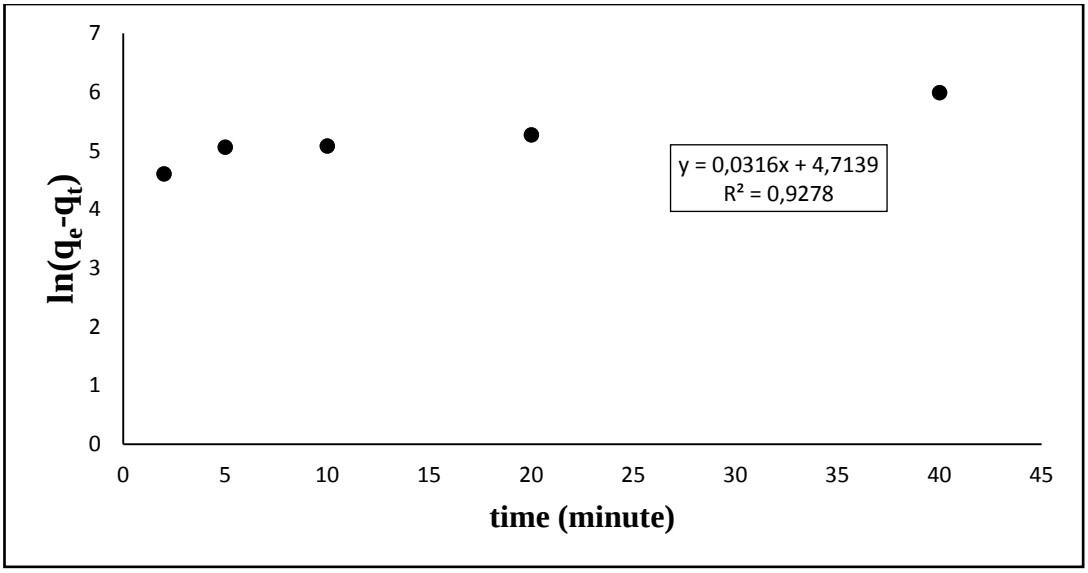

Figure 4.9 The pseudo 1st order model plots of Hg (II) adsorbed by the Resin 2

The pseudo-second-order kinetic model assumes that the rate limiting step is the interaction between two reagent particles [88].

This model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k^2 q_e^2} + \frac{t}{q_e} \qquad \textbf{(4.2)}$$

where k_2 is the constant of pseudo-second-order rate (g/mg min), and q_t is the adsorption amount at time t. Plotting t/q_t vs t, straight lines were obtained (Figure 4.6). And the constant k_2 and q_e values for Hg (II) was calculated and shown in Table 4.4. Accordance with the pseudo-second-order reaction mechanism, the overall rate of Hg (II) adsorption processes appears to be controlled by the chemical processes, through sharing of electrons between adsorbent and adsorbate, or covalent forces, through the exchange of electrons between the particles involved.

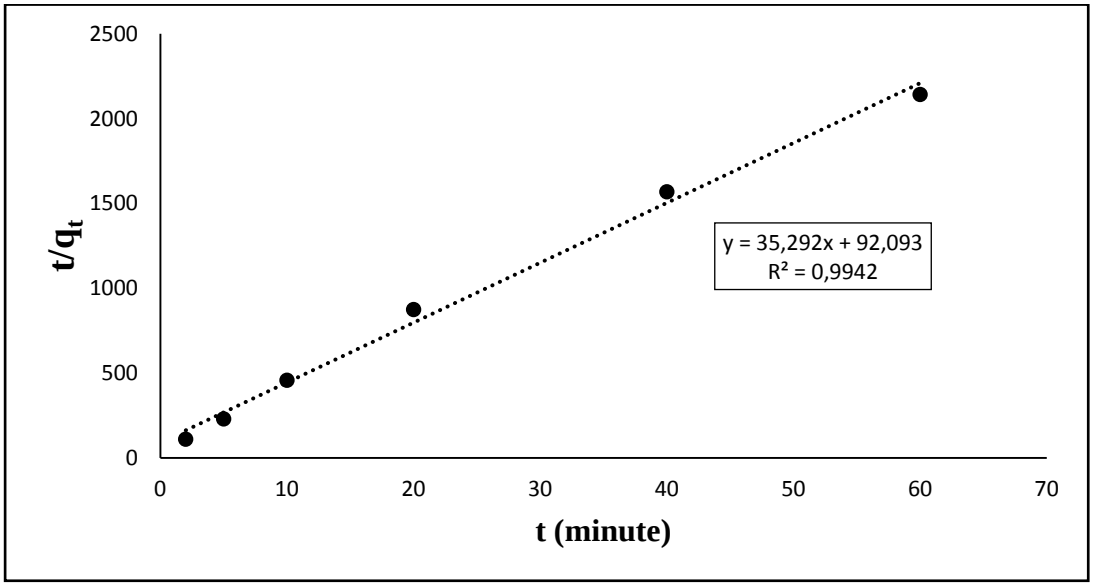

Figure 4.10 The pseudo 2nd order model plots of Hg (II) adsorbed by the Resin 2

To examine the nature of the diffusion process for the adsorption of mercury onto the resin attempts were made to calculate the pore diffusion coefficients [89] as intra-particle transport is supposed to be the rate-controlling step [90] In the intra-particle diffusion model proposed by Weber and Morris, [84] the initial rate of intra-particular diffusion is calculated by linearization of the curve:

$$q_t = f\,(t^{1/2}) \qquad \textbf{(4.3)}$$

where K_i is the diffusion coefficient in the solid (mg g^{-1} $min^{-1/2}$). The values of intra-particle diffusion rate constant, K_i, are tabulated in Table 4.4.

If the regression of q versus $t^{1/2}$ is linear and passes through the origin, then intra-particle diffusion is the sole rate-limiting step. Figure 4.7 shows the plot of q_t versus $t^{1/2}$ for mercury adsorption. The deviation of the lines from the origin indicates that intra-particle transport is not the rate-limiting step.

Table 4.4 Parameters of the kinetic models of Hg (II) adsorption onto Resin 2.

q_{eq} exp	First Order			Second Order			Intra-particle Diffusion	
	k_1 (mmol g^{-1})	q_e (mmol.g^{-1})	R^2	k_2 (g $mmol^{-1}$ min^{-1})	q_e (mmol.g^{-1})	R^2	K_i (mmol g^{-1} $min^{-1/2}$)	R^2
0.030	0.728	$8.97x10^{-4}$	0,93	13.85	0.028	0,994	0,017	0,94

According to the data of Table 4.4, the pseudo-first-order kinetic model having a low value for R^2, does not present a good fit with experimental data. In contrast, in the case of pseudo-second-order kinetic model, the high values of correlation coefficients showed that the data fitted well to the pseudo-second-order rate kinetic mode.

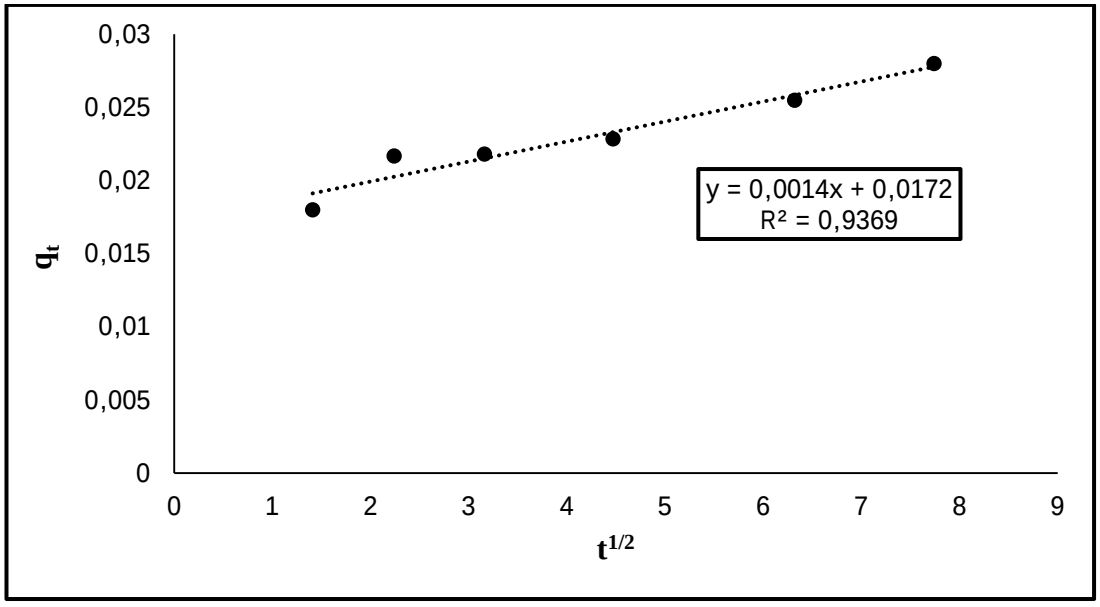

Figure 4.11 Intra-particular diffusion model plot of Hg (II) adsorbed by the Resin 2

4.6 Adsorption Isotherms Models

The adsorption isotherm was obtained from batch experiment at different temperatures. Three theoretical isotherm models viz. Langmuir [91], Freundlich [92] and Dubinin–Radushkevich [93] were used to analyze the experimental data.

Three theoretical isotherm models viz. Langmuir, Freundlich and Dubinin Radushkevich (D–R) models were used to analyze the experimental data.

4.6.1 Langmuir isotherm

One of the most widely used isotherm equations for modeling adsorption data is the Langmuir equation, which for dilute solutions may be represented as:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_E} \qquad \textbf{(4.4)}$$

In Eq. (4.4), *C*e is the equilibrium concentration of mercury in solution (mol/L), *q*e is the equilibrium amount of mercury adsorbed on the beads at time *t* (mmol/g). *q*m is the maximum adsorption capacity of the beads (mmol/g) and *b* (i.e., the adversely of dissociation constant of the ligand/surface interaction, K_d, or equal to association constant, K_a, ($b = K_a = (1/K_d)$) is the energy of adsorption dissociation constant. K_d has dimension of concentration, and the mercury binding is stronger when it is smaller.

The Langmuir model is based on the assumption of surface homogeneity such as equally available adsorption sites, monolayer surface coverage, and no interaction between adsorbed species. The corresponding semi-reciprocal plot (C_{eq}/q_{eq} versus C_{eq}) of the experimental data gave a linear plot for the beads. Since the Langmuir model is formulated for homogenous adsorption the adsorption of mercury onto the beads can be described in terms of this model.

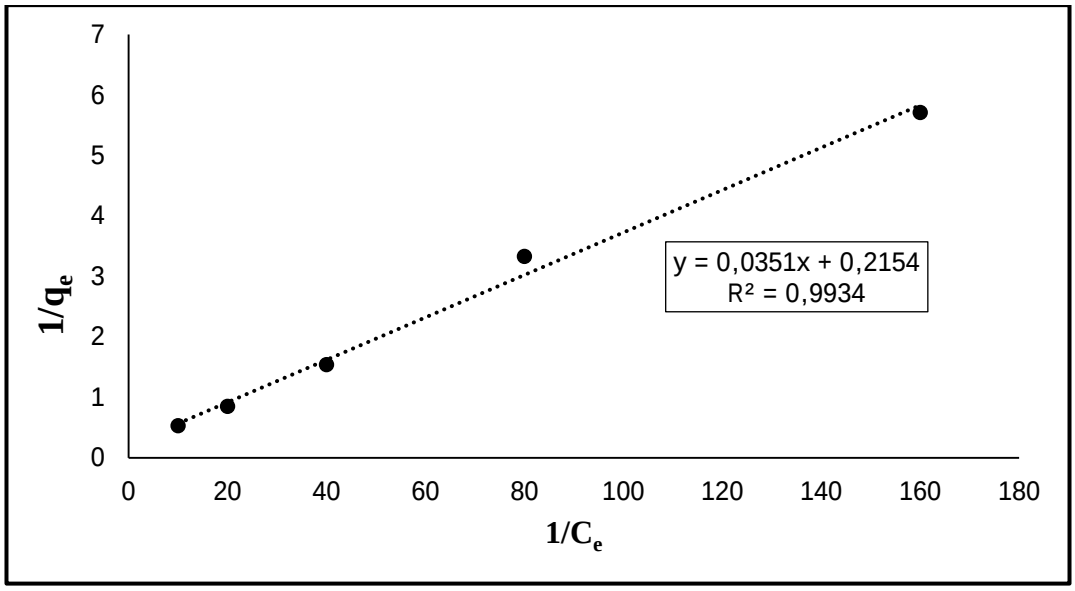

Figure 4.12 Langmuir Isotherm Model

4.6.2 Freundlich isotherm

The Freundlich expression is an empirical equation based on adsorption on a heterogeneous surface. The Freundlich equation is commonly presented as:

$$q_e = K_F C_e^{1/n} \quad \textbf{(4.5)}$$

where K_F and n are the Freundlich constants characteristic of the system. K_F and n are indicator of the adsorption capacity and adsorption intensity, respectively. The slope and the intercept of the linear Freundlich equation are equal to $1/n$ and ln K_F, respectively.

The linear plots of ln q versus ln$C$ showed that the Freundlich isotherm can be representative for the mercury adsorption. The magnitude of K_F and n values of Freundlich model showed easy uptake of mercury from aqueous medium with a high adsorption capacity of the beads at room temperature. Values of n>1 for affinity beads indicates positive cooperativity in binding.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \textbf{(4.6)}$$

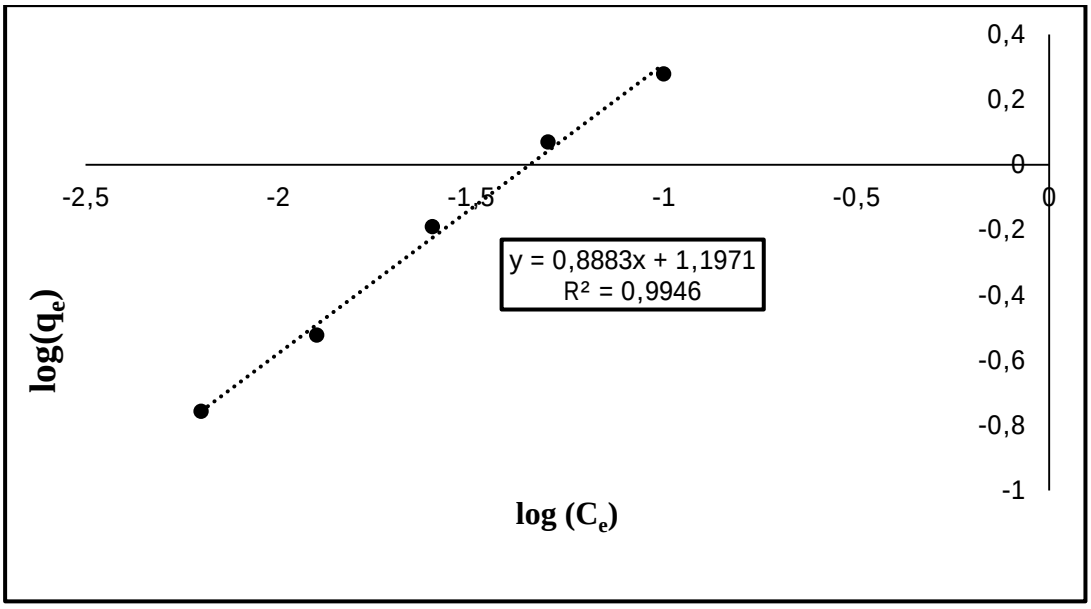

Figure 4.13 Freundlich Isotherm Model

4.6.3 Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich (D–R) isotherm is also widely used in adsorption studies because it does not assume a homogeneous surface or constant adsorption potential [93]. The D–R equation is given by the following relationship:

$$\ln(q_e) = \ln(q_s) - k_{ad}\varepsilon^2 \quad \textbf{(4.7)}$$

where q_e is the amount of the mercury adsorbed at the equilibrium, k is the constant related to the mean free energy of sorption, q_s is the theoretical saturation capacity, and ε is the potential, equal to $RT \ln(1 + (1/C_e))$. The values of q_s and k can be obtained by plotting ln q_e versus ε^2. The constant (k) is related to the mean free energy of adsorption per mole of the adsorbate as it is transferred to the surface of the solid from infinite distance in the solution, and the mean free energy (E) can be computed using the following relationship [93]. The Dubinin–Radushkevich (D–R) constant can give the valuable information regarding the mean energy of adsorption by the following equation:

$$E = (2k)^{-1/2} \quad \textbf{(4.8)}$$

The adsorption behavior might be predicted the physical adsorption in the range of 1–8 kJ/mol of the mean adsorption energies (E), and the chemical adsorption in more than 8 kJ/mol of the mean adsorption energies (E) [35]. D–R isotherm and parameters of mercury adsorption were presented in Figure 4.10 and Table 4.5,

respectively. *E* value was calculated as 2.016 kJ/mol for mercury, and found to be in the range of a typical free energy attributed to physical adsorption. So, the D–R isotherm also is a model which describes the experimental data compared to other applied isotherm models.

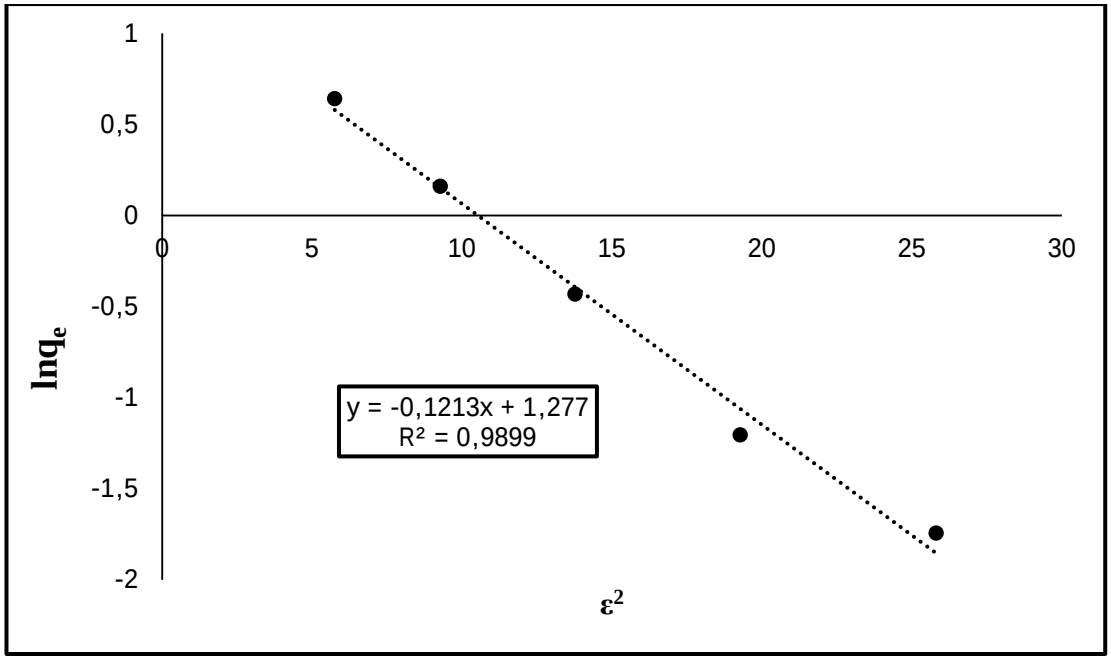

Figure 4.14 Dubinin–Radushkevich Isotherm Model

Table 4.5 Parameters of the adsorbtion isotherm models of Hg (II) adsorption onto Resin 2

Langmuir			**Freundlich**			**Dubinin–Radushkevich**			
Q_0	b	R^2	K_f	n	R^2	q_s	k_{ad}	R^2	E (kJ/mol)
4.64	6.14	0.9934	15.74	1.126	0.9946	3.586	0.1213	0.9899	2.016

5. CONCLUSION

The new sulfonamide based resins were prepared starting from crosslinked chlorosulfonated polystyrene (CSPS). Resin 1 was synthesized from starting from reaction with tris (2-aminoethyl) amine and CSPS resin. The resin 1 was interacted with excess of acetyl chloride to obtain the new sulfonamide-amide resin (resin 2).

The resin 2 is effective to remove of mercury ions from water. Under non-buffered conditions, the mercury uptake capacity is around 1.90 mmol/g resin.

Mercury uptake capacity of the resin 2 depends on pH. Mercury sorption capacity of the resin 2 is about 4.33 mmol/g resin at pH 6.

Mercury sorption kinetics of the resin 2 was studied and pseudo second order model was found suitable.

Adsorption isotherm model also was applied to the resin 2 and Langmiur isotherm model is suitable.

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